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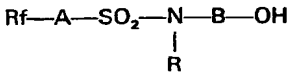
(54) Composition and process for the protection of materials against soiling

(57) A liquid composition for the protection of materials against soiling comprises by weight:

(A) 0.1% to 1% of at least one fluorinated resin based on an acrylic or methacrylic ester of a fluorinated sulfonamido-alcohol of general formula:



(I)

in which Rf is perfluoroalkyl, A is a direct bond or alkylene, B is alkylene and R is hydrogen or an alkyl, cycloalkyl, hydroxyalkyl or substituted or unsubstituted aryl radical, optionally with non-fluorinated monomer,

(B) 0.4% to 10% of at least one melamine-based aminoplast resin, thermoplastic resin or wax, and

(C) 89% to 99.5% of at least one organic solvent.

GB 2 077 274 A

Certain of the chemical formulae appearing in the printed specification were submitted in formal form after the date of filing.

SPECIFICATION

Composition and process for the protection of materials against soiling

The present invention relates to a composition and a process for the protection of materials against soiling.

The materials may be, for example walls, frontages, monuments, or sculptures in cement, brick, concrete or natural or reconstituted stone, material used for roof covering or construction material of wood, plastics or metal which are capable of being damaged or spoiled.

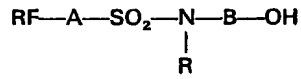
The damaging or spoiling may result from a natural process (e.g. deposits of dirty marks or stains or atmospheric dusts with eventual development of vegetable mosses, splashes of mud possibly with oily spots of petroleum origin or bird droppings) or an artificial process (e.g. unlicensed bill-sticking, inscriptions, or spraying of coloured liquid paints.

It is known that fluorinated resins based on acrylates or methacrylates of fluorinated alcohols considerably modify the adhesive properties of polar or non-polar liquids. Although their application in organic solution to the materials mentioned above confers on the latter some protection against natural or artifical soiling, this is not sufficient and the same applies to thermosetting or thermoplastic resins and waxes.

We have now found a composition which when applied to the above-mentioned materials confers on them, without alteration of modification of their initial appearance, complete protection against spoiling or at least to a large extent facilitates their cleaning so that the time needed for their restoration is considerably reduced.

According to the present invention composition for the protection of material against soiling is provided which comprises by weight:

(A) 0.1% to 1% of at least one fluorinated resin based on an acrylic or methacrylic ester of a fluorinated sulfonamido-alcohol, optionally with up to 80% of at least one non-fluorinated monomer, the fluorinated sulfonamido-alcohol having the general formula:



(I)

in which Rf represents a perfluoroalkyl radical, A represents a direct bond or and alkylene bridge, B represents an alkylene bridge and R represents a hydrogen atom or an alkyl, cycloalkyl, hydroxyalkyl or substituted or unsubstituted aryl radical,

(B) 0.4% to 10% of at least one melamine-based aminoplast resin, thermoplastic resin or wax, and

(C) 89% to 99.5% of at least one organic solvent.

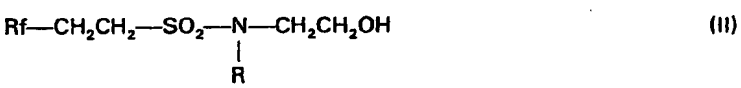
The invention includes a process for the protection of material against soiling in which a composition according to the invention is applied to the material.

In formula (I), the perfluoroalkyl radical may be straight or branched and contain for example 1 to 20 (preferably 4 to 16) carbon atoms; preferably, the alkylene bridge represented by A contains 2 or 4 carbon atoms and that represented by B contains 2 to 4 carbon atoms; the alkyl radical preferably contains 1 to 10 carbon atoms, the cycloalkyl radical 5 to 12 carbon atoms and the hydroxyalkyl radical 2 to 4 carbon atoms; the aryl radical (for example phenyl) may be substituted by an alkyl radical containing 1 to 6 carbon atoms.

Preferred non-fluorinated monomers are alkyl, hydroxyethyl, hydroxypropyl or glycidyl acrylates or methacrylates, acrylic acid, methacrylic acid, acrylamide or N-methylolacrylamide or mixtures thereof.

The fluorinated resins (A) used are preferably those which result from the polymerisation of at least one acrylic or methacrylic ester of a fluorinated alcohol, possibly accompanied by a minor proportion (e.g. up to 20%) of at least one non-fluorinated monomer, in the presence of a homopolymer or copolymer of non-fluorinated alkyl acrylate or methacrylate, or those which result from the polymerisation of at least one non-fluorinated alkyl acrylate or methacrylate, accompanied possibly by a minor proportion (e.g. up to 20%) of at least one other non-fluorinated monomer, in the presence of a homopolymer or copolymer based on an acrylic or methacrylic ester of at least one fluorinated alcohol.

Among these resins which are described in British Patents Nos. 1,413,995 and 1,543,084, those which are particularly interesting are those which are obtained by using on the one hand a non-fluorinated alkyl acrylate or methacrylate containing 1 to 20 carbon atoms in the alkyl radical and, on the other hand, an acrylic or methacrylic ester of at least one fluorinated alcohol of the general formula:



(II)

in which Rf and R have the same significance as above.

These fluorinated resins are generally obtained in the form of solutions in an inert organic solvent.

These solutions can be used so that in order to obtain a composition according to the present invention, it is sufficient to add thereto the quantities of adjuvant (B) required and possibly of an organic solvent (C). The organic solvent possibly added may be the same as that in the solution of the fluorinated resin or it may be different.

Examples of melamine-based aminoplast resins are the methyl or butyl ethers of hexamethylolmelamine and, preferably, the hexamethyl ether of hexamethylolmelamine. Among the compositions according to the invention, those which are particularly interesting contain 5% to 10% of aminoplast resin, this proportion being the greater as the porosity of the material to be treated is the higher. In order to assist the polymerisation of these resins, the composition according to the invention may contain a catalyst miscible or dispersible in an organic medium, preferably lactic acid, in a portion of 2% to 10% with regard to the weight of aminoplast resin employed.

The thermoplastic resins and the waxes, preferably employed in a proportion of 0.4% to 5%, may be used alone or, advantageously, in admixture with an aminoplast resin for treating materials having a high porosity.

Examples of thermoplastic resins which may be used are polyvinyl resins, especially those based on polyvinyl chloride, epoxy resins especially those derived from bisphenol and epichlorhydrin, modified or unmodified polyester resins, styrene resins or other alkyd copolymers, polymethyl styrenes and acrylonitrile-styrene copolymers, acrylic resins (e.g. polyacrylates or polymethacrylates, especially methyl, ethyl, butyl or cyclohexyl polymethacrylates), alkyd-urethane resins, as well as phenol resins which are miscible or dispersible in an organic medium. When a cross-linkable thermoplastic resin, for example, an epoxy resin or an acrylic resin, is used the composition according to the invention may possibly also contain a catalyst customarily used to assist the cross-linking during drying.

The preferred waxes are the paraffins, the paraffin oils and the stearins. One at least of these products is advantageously used when the composition according to the invention is intended for the protection of materials with a high porosity e.g. concrete, natural or reconstituted stone or baked clay. On the other hand their use is sometimes to be avoided when the composition according to the invention is to used for the protection of a metal surface whether painted or not since they can initiate corrosion phenomena. The parraffins can be used in the form of "extenders", for example the mixtures of paraffins and stearyl alcohol phosphates condensed on aluminium isopropylate (British Patent No. 1,089,576) or mixtures of paraffins and aluminium stearates in the presence of methylcyclohexanol.

The choice of organic solvent to be used in the compositions according to the invention depends on numerous factors, especially the type of material to be protected (smooth or porous), its state (dry or damp) at the time of application, the appearance of the surface and the desired penetration, as well as the method of application and the desired speed of drying. Chlorinated solvents can be used such as for example trichloroethylene, perchlorethylene and above all 1,1,1-trichlorethane on account of its low toxicity, chlorofluoro solvents such as for example trichloromonofluoromethane, the difluorotetrachloroethanes, the trifluoro-trichloroethanes (preferably 1,2,2-trifluoro-1,1,2-trichloroethane) on account of their great speed of evaporation and their extremely low toxicity. If it is desired to increase the penetration of the compositions according to the invention on certain materials (e.g. hard woods, plastics or certain stones), than a ketone, in particular methylethylketone which can also play the role of third solvent, or an ester e.g. ethyl acetate, butyl acetate or amyl acetate may advantageously be used. On account of their low rate of evaporation which is of interest when they are to be applied by spraying, or their role of third solvent one can use aliphatic or aromatic hydrocarbons such as for example, petroleum hydrocarbons, white spirit, toluene, benzene or xylene, preferably at the rate of 5% to 50% or even more with respect to the total volume of the solvents used.

If it is desired to increase the fungal or bactericidal protection of the materials then anti-cryptogamic agents or bactericides can be incorporated without convenience in the compositions of the present invention.

The compositions according to the invention can be deposited on the materials to be protected in at least by one layer by means of brushes, rollers or spraying apparatus. The rate of drying, in the open air, depends chiefly on the rate of evaporation of solvents used. To obtain a satisfactory protection, it is generally sufficient to use 100 to 500 ml (1 ml = $10^{-6}m^3$) of the composition according to the invention per square metre of surface to be protected, preferably 120 to 350 ml/m^2, so as to deposit from 0.5 to 3 g/m^2 of fluorinated resin (A) and 0.5 to 30 g/m^2 of adjuvant (B).

This small deposit on the surface allows the treated materials (phenomenon of adsorption-desorption) to breathe better, there is a minimal adherence of the natural or artificial spots or stains (absence of adherent effect) and the anti-adherence effect lasts a considerable time. Another advantage of the compositions of the invention resides in the absence of any colour so that, when they are only applied on a portion of a material to be protected (for example the lower part of a wall), one cannot see the demarcation between the treated part and the untreated part.

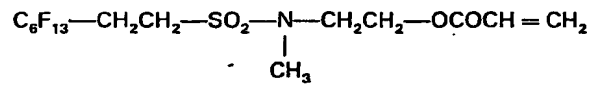
The invention is illustrated by the following Examples, in which the parts and percentages indicated are by weight unless the contrary is mentioned.

EXAMPLE 1

(a) *Preparation of the fluorinated resin*

76 parts of 1,1,1-trichloroethane, 18 parts of stearyl methacrylate, 2 parts of hydroxyethyl methacrylate and 0.2 parts of lauroyl peroxide dissolved in 4 parts of 1,1,1-trichloroethane are introduced into a reactor. After putting the reactor under an atmosphere of nitrogen, it is heated at 74°C for 3 hours with stirring.

A mixture of 20 parts of an 80% solution of fluorinated acrylate of the formula:



(III)

in acetone, 4 parts of stearyl methacrylate and 76 parts of 1,1,1-trichloroethane is introduced into the solution of non-fluorinated acrylic resin thus formed and then a solution 0.2 parts of lauroyl peroxide in 4 parts of 1,1,1-trichloroethane and the whole is heated for 4 hours at 74°C with stirring. After dilution with 176 parts 1,1,1-trichloroethane, a solution of about 10.5% of fluorinated resin in 1,1,1-trichloroethane is thus obtained (referred to below as "Solution RF_1").

(b) *Composition according to the invention*

The following ingredients:

. 1,1,1-Trichloroethane	130 parts
. Lactic acid (d = 1.21)	1 "
. Hexamethyl ether of hexamethylolmelamine (99 ± 1% of active materials)	12 "
.. Solution RF_1	4 "

are introduced successively into a mixer with gentle stirring either at the ambient temperature, or preferably at 35—40°C.

After complete dilution of these ingredients, a composition is obtained according to the invention, in the form of a clear homogeneous liquid or density approximately 1.4 containing about 0.3% of fluorinated resin, 8.1% of the hexamethyl ether of hexamethylolmelamine, 90.9% of 1,1,1-trichloroethane and 0.7% of lactic acid.

This composition can be applied with a brush or paint brush or by spraying at the rate of 250 to 300 ml/m² to materials such as bricks, stones and concrete, the drying and the polymerisation being effected in the ambient air.

Analogous compositions are obtained if solution RF_1 is replaced by one of the compositions described in Examples 1 to 11 of British Patent No. 1,543,084 or by a solution of one of the products described in Examples 1 to 5 of British Patent No. 1,413,995 employing the same proportions of active materials.

EXAMPLE 2

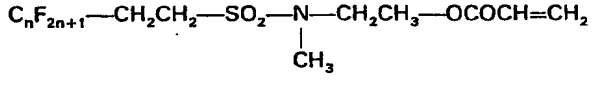
Two mixtures are separately prepared having the following compositions:

Mixture A		
	. 1,1,1-Trichloroethane	130 parts
	. Hexamethyl ether of hexamethylolmelamine (99 ± 1% of active materials	12 "
Mixture B		
	. Lactic acid (d = 1.21)	1 part
	. Solution RF_1	4 "

These mixtures can be preserved for several days before they need to be used. When they are to be used mixture B is introduced with stirring into the mixture A to obtain a composition according to the invention which may be applied as in the preceding Example.

EXAMPLE 3

The operation is as in Example 1 or 2, with the exception that solution RF_1 is replaced by the same quantity of a solution prepared in the same way but by replacing the monomer of formula (III) by a mixture of seven fluorinated monomers of the formula:



(IV)

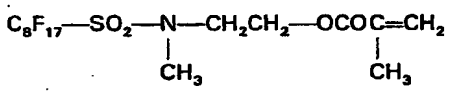
where n is equal to 4, 6, 8, 10, 12, 14 and 16 in the ratios of average weight respectively of

1:50:31:10:3:1:1.

The composition according to the invention thus obtained has properties analogous to those of Example 1 and can be applied in the same way.

EXAMPLE 4

The operation is as in Example 1, but the fluorinated resin used is a copolymer based on the fluorinated monomer of formula V set out below (57—60%), octadecyl methacrylate (27%), hexadecyl methacrylate (8.5%) and other methacrylates of non-fluorinated C_{14}, C_{16} and C_{20} alcohols (3—6%).



(V)

EXAMPLE 5

The following ingredients are successively introduced in a mixer with gentle stirring and at —40°C:

. 1,1,1-Trichloroethane	115 parts
. White spirit (less than 5% of aromatic compounds)	15 "
. Catalyst containing 70% of ethanol, 15% of ethyleneglycol and 15% of hydrochloric acid (d = 1.18)	1 "
. Hexamethyl ether of hexamethylolmelamine (99±1% of active materials)	9 "
. Solution RF_1	6 "

After complete dilution of these ingredients, a composition is obtained according to the invention, in the form of a clear homogeneous liquid, containing about 0.4% of fluorinated resin, 6.2% of the hexamethyl ether of hexamethylolmelamine, 82.5% of 1,1,1-trichloroethane and 10.2% of white spirit.

This composition can be applied at the rate of 250 to 300 ml/m² to different materials, notably on to cork and wood agglomerates.

EXAMPLE 6

The following ingredients are successively introduced into a mixer:

. Perchlorethylene	170 parts
. Solution of polystyrene (40% of active materials) in perchlorethylene	2 "
. Solution RF_1	7 "

After complete dilution a composition is obtained according to the invention, in the form of a liquid which is stable on storage, (for more than one year), containing about 0.4% of fluorinated resin, 0.45% of polystyrene, 95.65% of perchloroethylene and 3.5% of 1,1,1-trichloroethane.

This composition, which is principally intended for the protection of objects based on natural or reconstituted stone (e.g. flat basins, jardinieres, statues), can be applied to these objects with a brush in one or two layers at the rate of 150 to 300 ml/m² according to the degree of protection desired.

The objects thus protected possess a better behaviour in frosty weather owing to their smaller absorption of moisture. Moreover natural contaminations become incrusted thereon less easily and can be removed by a simple brushing with cold water. The presence of polystyrene in the composition confers on the facing a better adherence and an excellent stability.

EXAMPLE 7

The following ingredients are successively introduced into a mixer with stirring and at the ambient temperature:

. 1,1,1-Trichloroethane	90 parts
. Benzene or toluene	50 "
. Solution (35%) of polyvinylchloride in cyclohexanone	5 "
. Solution RF_1	10 "

After complete dilution a composition according to the invention is obtained containing about 0.7% of fluorinated resin, 1.1% of polyvinylchloride, 63.8% of 1,1,1-trichloroethane, 32.3% of benzene and 2.1% of cyclohexanone, intended more particularly for the protection of porous materials exposed to the weather and used, for example, for the coating of roofs e.g. bituminous slates, shingles, clay tiles. The application can be carried out with a roller or by spraying at the rate of 250 to 300 ml/m².

By contrast with the application of the fluorinated resin alone, a reinforcement of the water-repellent effect and reduced penetration is noted and therefore an increase in the surface protection; the picking up of atmospheric dust is less and the development of vegetable mosses is found to be much reduced, even on faces exposed to the north.

EXAMPLE 8

The operation is as in the preceding Examples but using the following ingredients:

. Methylethylketone	15 parts
. Solution (50%) of methyl polymethacrylate in methylethylketone	10 "
. 1,1,1-Trichloroethane	120 "
. Hexamethylether of hexamethylolmelamine (at 99 ± 1% of active materials)	10 "
. Solution RF_1	15 "

The composition according to the invention thus obtained which contains about 0.9% of fluorinated resin, 2.9% of methyl polymethacrylate, 5.9% of the hexamethyl ether of hexamethylolmelamine, 11.8% of methylethylketone and 78.5% of 1,1,1-trichloroethane, is present in the form of a homogeneous liquid which can be applied to the materials to be protected at the rate of 170 to 250 ml/m².

EXAMPLE 9

The operation is as in the preceding Examples but using the following ingredients:

. White spirits (less than 5% of aromatic compounds)	80 parts
. Solution (75%) of an alkyd resin (68% of fatty acid of tall-oil) in white-spirit	5 "
. Solution RF_1	5 "

The composition according to the invention thus obtained contains about 0.6% of fluorinated resin, 4.1% of alkyd resin, 90.3% of white-spirit and 5% of 1,1,1-trichloroethane, and can be applied at the rate of 120 to 200 ml/m² to the materials to be protected.

EXAMPLE 10

With gentle stirring, the following ingredients are successively mixed:

. Xylene	90 parts
. Solution (33%) of an unsaturated polyester resin, prepared from a 60/40 mass of polyester/styrene with a 50/50 mixture of xylene and ethyl acetate	8 "
. Solution RF_1	5 "

A composition according to the invention is obtained containing about 0.5% of fluorinated resin, 2.5% of polyester, 90% of xylene, 2.6% of ethyl acetate and 4.4% of 1,1,1-trichloroethane.

EXAMPLE 11

The following ingredients are mixed successively with moderate stirring and at the ambient temperature or preferably at 35—40°C:

. 1,1,1-Trichloroethane	120 parts
. Crude paraffin (melting point: 35°C)	8 "
. Hexamethyl ether of hexamethylol- melamine (99 ± 1% of active materials)	10 "
. Solution RF_1	4 "
. Trichloromonofluoromethane	40 "

A composition according to the invention is obtained containing about 0.2% of fluorinated resin, 4.4% of paraffin, 5.5% of the hexamethyl ether of hexamethylolmelamine, 67.9% of 1,1,1-trichloroethane and 22% of trichloromonofluororomethane in the form of a homogeneous liquid which can be applied at the rate of 200 to 300 ml/m² for the protection of concrete, stones or bricks.

EXAMPLE 12

The compositions according to the invention described in Examples 1, 2 and 11 (subsequently denoted compositions 1, 2 and 11) are applied to a wall consisting of plates or slabs of reinforced concrete, in comparison with the compositions A, B, C and D, which do not conform to the present invention, prepared in the same way from the ingredients indicated in the following Table (p = parts).

Ingredients	Composition A	Composition B	Composition C	Composition D
•1,1,1-Trichloroethane	130 p.	130 p.	120 p.	120 p.
•Crude paraffin (m.p.: 35°C)	—	—	8 p.	—
•Solution RF_1	4 p.	—	—	4 p.
•Lactic acid (d = 1.21)	—	1 p.	—	—
•Hexamethyl ether of hexamethylolmelamine (99 ± 1%)	—	12 p	10 p.	—
•Trichloromonofluoromethane	—	—	40 p.	40 p.

Compositions 1, 2, 11, A, B, C, and D are applied with a paint roller in two layers at the rate of 175 ml/m² for the first and 125 ml/m² for the second, with a period of intermediate drying of 3 hours. After the application of the second layer, it is left to dry in the ambient air for 24 hours, then the efficiency of the treatment and the protection of the concrete against unlicensed bill sticking.

For this purpose, the different portions of wall treated have been sized by means of adhesives based on methyl-cellulose and carboxymethylcellulose generally employed for sticking advertising bills. Three commercial adhesives have been separately tested.

Adhesive REMY in aqueous solution at 70 g/l
(Etab. REMY)
Adhesive QUELYD " " 70 g/l
(Etab. QUELYD)
Maxi adhesive GP " " 50 g/l
(Galeries du papier point)

Operating by the usual method followed by bill stickers, namely: uniform pasting of the concrete support by means of a brush soaked with adhesive, then applying the bill or poster and finally brushing the whole surface of the poster with the brush soaked with adhesive.

The ease of removal of the poster after 24 hours drying is estimated on the one hand by tests of removal when dry (tentative removal of the dry poster), on the other hand by tests of removal in the damp state (superficial rewetting of the poster by sprinkling with water, leaving for 15 minutes, then tentative removal). The ease of removal of a rectangular poster (1 m × 0.6 m) has been numbered as follows:

1 — very easy removal (less than 20 seconds for complete removal of the poster)
2 — easy removal (20 to 40 seconds)
3 — moderately easy removal (3 to 6 minutes)
4 — difficult removal (6 to 15 minutes)
5 — very difficult removal (15 to 30 minutes)
6 — complete removal practically impossible (tearing in thickness of the poster).

The following Table connects the results obtained:

Composition	REMY adhesive		QUELYD adhesive		MAXI adhesive GP	
	removal		removal		removal	
	DRY	DAMP	DRY	DAMP	DRY	DAMP
None (untreated wall)	5	3	5	3	6	2–3
A	2–3	3	2–3	3	3	3–4
B	5	4–5	5	4–5	5	5
C	2	2–3	3	2–3	4	4–5
D	2–3	3	2	2–3	2–3	3–4
1	1	1	1	1	1–2	1–2
2	1	1–2	1	1–2	1–2	1–2
11	1	1	1	1	1–2	1–2

These results show that the compositions according to the invention confer on the concrete supports an excellent anti-adherence effect, superior to that of compositions A, B, C and D corresponding to the elements of the compositions claimed taken separately.

EXAMPLE 13

Compositions 1, 2, 11, A, B, C and D defined above were applied to metal walls consisting of metal plates coated with a paint having an aluminium powder base. The application of the compositions was effected by spraying with two layers with intermediate drying in the ambient air, so as to deposit altogether 250 ml of composition per square metre of surface to be protected.

The removal tests were effected as in Example 12 with the same adhesives and after drying for 24 hours in the ambient air.

The results obtained are shown in the following Table.

Composition	REMY adhesive		QUELYD adhesive		MAXI adhesive GP	
	Removal		Removal		Removal	
	DRY	DAMP	DRY	DAMP	DRY	DAMP
None (untreated wall)	6	5	6	5	6	6
A	2–3	3	2–3	3	3	3
B	5	4	5–6	4–5	6	6
C	3	2–3	3	3	3–4	4
D	3	3	2–3	3	3	3
1	1	1	1	1	2	2
2	1	1	1	1	2	2
11	1	1	1	1	2	2

The best performances are obtained with the compositions 1, 2 and 11 according to the invention.

EXAMPLE 14

On a part of the wall of a cottage which was fully exposed to the East and which was faced with a coating of smooth mortar and covered for more than a year with a paint based on an emulsion of acrylic derivatives, composition 11, was applied with a paint roller in two successive layers with intermediate drying in the ambient air, so as to deposit 150 ml/m² in each layer.

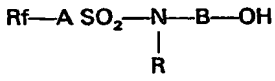
On two other parts of the same wall compositions C and D were applied in the same way.

It was found that composition 11 according to the invention conferred excellent protection on this wall, which was habitually soiled by the droppings of swallows which constructed their nests under the cornices of the roof. One sprinkling with a jet of water was sufficient to remove the contamination although with compositions C and D an energetic brushing is necessary to restore the wall to a fit state.

CLAIMS

1. A liquid composition for the protection of material against soiling which comprises by weight:

(A) 0.1% to 1% of at least one fluorinated resin based on an acrylic or methacrylic ester of a fluorinated sulfonamido-alcohol, optionally with at least one non-fluorinated monomer, the fluorinated sulfonamido-alcohol having the general formula:



(I)

in which Rf represents a perfluoroalkyl radical, A represents a direct bond or and alkylene bridge, B represents an alkylene bridge and R represents a hydrogen atom or an alkyl, cycloalkyl, hydroxyalkyl or substituted or unsubstituted aryl radical,

(B) 0.4% to 10% of at least one melamine-based aminoplast resin, thermoplastic resin or wax, and

(C) 89% to 99.5% of at least one organic solvent.

2. Composition according to claim 1 in which the fluorinated resin (A) results from the polymerisation of at least one acrylic or methacrylic ester of a fluorinated alcohol (I), optionally accompanied by a minor proportion of at least one non-fluorinated monomer, in the presence of a homopolymer or copolymer of non-fluorinated alkyl acrylate or methacrylate.

3. Composition according to claim 1 in which the fluorinated resin (A) results from the polymerisation of at least one non-fluorinated alkyl acrylates or methacrylates optionally accompanied by a minor proportion of at least one other non-fluorinated monomer, in the presence of a homopolymer or copolymer based on acrylic or methacrylic ester of at least one fluorinated alcohol (I).

4. Composition according to claim 1, 2 or 3 in which Rf represents a straight or branched perfluoroalkyl radical containing 1 to 20 carbon atom and R represents a hydrogen atom, an alkyl radical containing 1 to 10 carbon atoms, a cycloalkyl radical containing 5 to 12 carbon atoms, a hydroxyalkyl radical containing 2 to 4 carbon atoms or an aryl radical optionally substituted by an alkyl radical containing 1 to 6 carbon atoms.

5. Composition according to any of claims 1 to 4 in which Rf contains 4 to 16 carbon atoms.

6. Composition according to any of claims 1 to 5 in which R represents phenyl.

7. Composition according to any of claims 1 to 6 in which A contains 2 or 4 carbon atoms.

8. Composition according to any of claims 1 to 7 in which B contains 2 to 4 carbon atoms.

9. Composition according to any of claims 2 to 8 in which the alkyl radical of the non-fluorinated alkyl acrylate or methacrylate contains 1 to 20 carbon atoms.

10. Composition according to any of claims 1 to 9 in which (B) is an aminoplast resin present in an amount of 5% to 10%.

11. Composition according to claim 10 containing a polymerisation catalyst in an amount of 2% to 10% based on the weight of aminoplast resin.

12. Composition according to any claims 1 to 11 in which (B) is the hexamethyl ether of hexamethylolmelamine.

13. Composition according to any of claims 1 to 12 in which (B) is a polyvinyl resin, epoxy resin, polyester resin, styrene resin, acrylic resin, alkyd-urethane resin or phenolic resin.

14. Composition according to claim 13 in which the resin is present in an amount of 0.4% to 5%.

15. Composition according to claim 13 or 14 in which (B) is an epoxy or acrylic resin and a cross-linking catalyst is present.

16. Composition according to any of claims 1 to 15 in which (B) is a paraffin wax, paraffin oil or stearin.

17. Composition according to claim 16 in which the wax is present in an amount of 0.4% to 5%.

18. Composition according to any of claims 1 to 17 in which the solvent is a chlorinated solvent, chlorofluorinated solvent, a ketone, an ester, an aliphatic hydrocarbon or an aromatic hydrocarbon.

19. Composition according to any of claims 1 to 18 in which the solvent is 1,1,1-trichloroethane or 1,2,2-trifluoro-1,1,2-trichloroethane.

20. Composition according to any of claims 1 to 19 which comprises in addition at least one anticryptogamic or bactericidal agent.

21. Composition for the protection of material against soiling substantially as herein described with reference to and as illustrated in any of Examples 1 to 11.

22. Process for the protection of material against soiling in which a composition according to any of claims 1 to 21 is applied to the material.

23. Process according to claim 22 in which the composition is applied at the rate of 100 to 500 ml of composition per square metre of surface to be protected.

24. Process according to claim 23 in which the composition is applied at the rate of 120 to 350 ml per square metre of surface to be protected.

25. Process for the protection of material against soiling substantially as herein described with reference to and as illustrated in any of Examples 12 to 14.

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